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XII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

THE ANALYSIS OF CUPRIC BROMIDE, AND THE ATOMIC WEIGHT OF COPPER.

By Theodore William Richards.

Presented by the Corresponding Secretary, October 8, 1890.

Introduction.

The uncertainty of knowledge regarding the atomic weight of copper, owing to the widely different values assigned by various experimenters, led nearly four years ago to the beginning of an investigation, of which this paper is the third publication. The two earlier papers * described a number of determinations made by a method which had not until then been successfully applied, — the precipitation of metallic silver from neutral silver solutions by means of metallic copper. The results obtained were in themselves very satisfactory, but differed entirely from the value which has hitherto been accepted with little question by chemists; and the desire to discover, if possible, the cause of this discrepancy, has finally led to the continuance of the investigation.

It is well known that we can rarely find with regard to any element more than one or two compounds which answer the exacting requirements of atomic weight determination; although others of its definite compounds may by their analysis more or less strongly support the verdict of the more exact results. Disagreement implies constant error in one or other of the disagreeing values, and the detection and correction of this constant error can alone give certainty to our conclusions. Much, however, may be learnt by careful study from a new standpoint, and the first step in the present investigation was to discover if possible such an opening.

The basic tendency of cupric salts, and the ready oxidation of cuprous compounds, complicate to such an extent the relations of copper, that the preparation of any one of its salts in a dry state

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* These Proceedings, xxii. 342, and xxiii. 177; also Fresenius's Zeitschrift, xxviii. 392.

of perfect purity may be regarded as almost an impossibility. One by one the usual cupric and cuprous compounds were rejected as unsuitable for the foundation of a new research, until finally, after much study, cupric bromide was selected on account of the simplicity and exactness of its analysis, and moreover because by establishing beyond doubt the relation of copper to bromine we connect its atomic weight with precise values previously determined in this laboratory.

The balance used throughout the research was the one used by Professor Cooke in his admirable work upon the atomic weight of antimony, and was kindly loaned by him for the present purpose. A long-armed balance of the best type, manufactured by Becker of New York, it was very perceptibly turned by one twentieth of a milligram with a load of fifty grams in each pan, and showed unusual constancy in its indications. It was kept in a large quiet room of nearly constant temperature, and was protected from unequal heating and from air currents by suitable curtains. The weights were made by Sartorius in Göttingen, the larger ones being of gold-plated brass, and the fractions of a gram of platinum. Three days were spent in their comparison, according to a method somewhat similar to that described by Crookes,* and the very small corrections thus found were tabulated and applied to all results.

Before weighing, every object was allowed to remain in a desiccator near the balance, for at least seven hours. Every weight was determined at least thrice, each time according to a different method of swinging, and all precautions for accuracy were taken which are usual in such work. In the first experiments the weighings were made by substitution, but the conditions were so uniformly constant and the balance so manifestly reliable that this procedure seemed a useless expenditure of time. In fact, the probable error of the ordinary method of weighing under such circumstances is very much less than other possible errors of an investigation like the present. It is certain that the total inaccuracy of any weighing, due to all possible causes combined, could not have exceeded seven or eight one-hundredths of a milligram, and was without doubt usually very much less than that quantity. All weighings were of course reduced to a vacuum standard, allowing for the air displaced by the weights. Since these were standardized with reference to a brass ten-gram piece, it is evident that the fractions of a gram must be calculated as brass, and not as platinum.

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* Fresenius's Zeitschrift, vi. 431.

I. Preliminary Work.

Preparation and Analysis of Hydrobromic Acid.

The next step taken was the preparation of hydrobromic acid pure enough to serve as the basis of research. The acid was made from pure potassic bromide and sulphuric acid, according to the method recommended by Dr. Squibb.* It was then purified by repeated fractional distillation, at first in a large platinum retort, and afterward in one of glass; it having been ascertained that the gold used as a solder in the former apparatus was attacked during the process. It was subsequently found that the action of the acid even upon glass was not imperceptible, but as the same retort was used in all later distillations, and as the glass was of good quality, this unavoidable cause of impurity was reduced to a minimum.

The acid was distilled in all ten times, — seven times over potassic bromide, twice over silver bromide, and once alone, — each time the first and last portions of the distillate being rejected. A specimen of the wholly colorless product was preserved for over a year without perceptible change.

The necessity of testing the purity of this hydrobromic acid led at once to the next step of the investigation, the preparation of chemically pure silver. Fused argentic nitrate was first made from pure silver which had been reduced from the chloride by milk sugar and potash. This salt was then dissolved in a large amount of water, and again decomposed by the gradual addition of very dilute hydrochloric acid in slight excess, the precipitate being thoroughly agitated and washed by decantation with dilute hydrochloric acid and hot and cold water. After drying and pulverizing, the pure argentic chloride was digested for six hours with aqua regia, and then again washed with the purest hot and cold water until the filtrate gave no test for chlorine.

The final reduction of the cream-colored product was accomplished as before, by warming it with a dilute solution of the purest caustic potash and milk sugar, which had previously been filtered through a Gooch crucible. Careful testing showed the completion of the reaction, and the resulting pure silver, having been thoroughly washed with dilute sulphuric acid and a very large amount of pure hot water until perfectly clean, was collected and dried upon a quantitative filter. Small portions of the powder were successively supported upon a carbon dish similar to that described by Professor Cooke,* and, after being fused by means of a blowpipe directed downwards, the silver was allowed to cool in a reducing flame. The buttons were hammered upon a clean anvil, scrubbed with sand, rolled out between two plates of pure silver, cut with a hard steel chisel, boiled successively with hydrochloric acid and ammonia, scrubbed once more with sand, and, after heating with melted potassic hydrate in a silver crucible, finally scrubbed, washed, and dried.

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* These Proceedings, xvii. 30.

In order to prove the absence of any absorbed gases in the resulting metal the following experiments were made.

I. 1.3412 grams of silver heated in vacuo to a low red heat weighed after cooling 1.3412 grams.

II. 1.5763 grams after being subjected to the same treatment weighed 1.5763 grams.

The absolute constancy of these weights is sufficient proof of the point in question. The silver yielded a perfectly clear solution upon treatment with nitric acid and subsequent addition of water, and gave every evidence of being chemically pure.

In order to determine the purity of the hydrobromic acid previously made, the solution of a known weight of the pure silver described above was decomposed by a slight excess of this liquid, and the resulting precipitate was weighed. The metal was dissolved in a very slight excess of warm pure nitric acid diluted with two volumes of water, the whole being contained in the half-litre Erlenmeyer flask which was afterward to serve for the precipitation. The very small amount of gas formed by the decomposition of the nitric acid was forced to pass through a zigzag tube provided with bulbs, in order that the infinitesimal amount of spray might be retained. The tube apparatus was not ground into the flask, but fitted only with moderate tightness, the joint being sealed by water held in place by capillary attraction. After the complete solution of the silver, the contents of the flask were gently boiled to drive off the lower oxides of nitrogen, and the whole was diluted to about two hundred cubic centimeters. To this hot liquid was added very gradually the least possible excess of a dilute solution of known strength made from the hydrobromic acid above described, and the mixture was constantly and violently shaken, the flask being closed with a smooth rubber stopper. After settling, the precipitate was thoroughly washed with hot water, and collected in a

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* These Proceedings, xvii. 17.

Gooch perforated crucible with all possible care. The crucible with its contents was dried at 130° to constant weight, and showed no loss in any case on additional heating to 180°.

SYNTHESES OF ARGENTIC BROMIDE.

No. of Experiment.	Silver taken (reduced to Vacuum).	AgBr formed (reduced to Vacuum).	Percentage Ag in AgBr.
	grams.	grams.	
1	1.11235	1.93630	57.447
2	1.57620	2.74335	57.455
3	2.16670	3.77170	57.446
		Average. . . .	57.449
		According to Stas . . .	57.445

The above variation is not greater than a possible error in the operations concerned, and the testimony which these results give to the purity of the materials is sufficient for the present purpose. Other experimenters in this Laboratory have obtained values ranging from 57.442 to 57.450.

Preparation of Cupric Bromide.

The salt used in the preliminary series of experiments upon the atomic weight of copper was formed by the solution of the purest obtainable cupric oxide in the hydrobromic acid which has been described above. For the preparation of the oxide of copper pure electrolytic metal (of the quality used in the experiments published three years ago) was converted into sulphate by means of pure nitric and sulphuric acids, and the resulting salt was purified by six fractional recrystallizations after the expulsion of the remaining nitric acid by heat. From a dilute solution of the purest cupric sulphate acidified with nitric and sulphuric acids, about half the metal was deposited upon the interior of a large platinum dish. The remaining liquid being decanted, the film was washed, redissolved, and partially redeposited through the agency of two Bunsen cells. It was hoped that this fractionation would rid the copper of that probable impurity which almost invariably manifests itself as minute dark spots upon the surface of the film of a completed electrolysis, but the hope proved to be a vain one, and no method of purification was devised which would wholly remove the difficulty. Some of the copper films obtained in the course of the work were almost free from the minute spots, while others of the same series showed a larger number of them; but the phenomenon did not appear to affect the results. From this it would seem that the supposed impurity might have consisted merely of finely divided copper, but even on the worst supposition the amount was so infinitesimal that it could have had no influence upon the observed atomic weight.

The brilliant metallic film thus prepared was carefully separated from the platinum and thoroughly washed with hot water. The separation of the copper from the dish is greatly facilitated by previously rubbing the surface of this electrode with an exceedingly small quantity of pure semi-liquid paraffin, which seems to fill the microscopic cavities of the platinum without interfering with the continuity of the copper film. The pure washed copper was returned to the clean dish, dissolved in very pure nitric acid, and the product slowly converted into basic nitrate, and finally into oxide, by gradually increasing heat. The last part of the operation was conducted at a low red heat in porcelain, and of the product only the central portions were used in the work. The resulting cupric oxide was a fine black powder, which dissolved completely in acids, and gave every evidence of being chemically pure.

A large quantity of this copper oxide was dissolved in a slight excess of pure hydrobromic acid, and the solution evaporated to dryness over a steam bath. Of course, every possible precaution against dust and other impurity was taken with regard to this as well as to every other operation of the research, neither hydrochloric acid nor ammonia being used in the room devoted to it. During the process of evaporation a very faint odor of bromine was perceptible; and upon the subsequent solution of the brilliant black scales of cupric bromide in water, the clear blue liquid slowly deposited a few microscopic crystals of the basic bromide, which will be described in another place. After standing a few days the crystals ceased to be deposited, and the filtered clear odorless solution remained for about four weeks without further change, serving as the basis of a number of experiments, and furnishing material for the first series of preliminary analyses.

Since it was evidently impossible to obtain the normal salt by the evaporation of the solution at 100° in the air, many attempts were made to prepare it by concentration of the neutral solution over sulphuric acid in air and in nitrogen gas of low tension. The first trials all ended in failure, and it was not until much later that the problem was successfully solved. The purest salt obtained at this stage of the work consisted of brilliant black crystalline scales, which, contrary to all expectation and all literature* upon the subject, were not very deliquescent unless moistened with strong hydrobromic acid. Since the normal compound invariably seems to lose a trace of bromine on exposure to the air, the lack of deliquescence may be due to a very thin superficial covering of the basic bromide. The normal salt is soluble in a very small amount of water, forming a brownish black solution; this becomes deep purple after the addition of hydrobromic acid, and upon gradual dilution goes through successive shades of brown and dirty green to a most beautiful "robin's egg" blue.

The basic salt above alluded to was found to be quite insoluble in water, hence it seemed probable that the dilute solution of cupric bromide from which it had separated was perfectly normal, and it became an important problem to settle this point. As the normal salts of copper are wholly without action upon a solution of methyl orange, this indicator formed the most convenient test for the neutrality of the liquid in question. To about fifty cubic centimeters of the clear solution of pure cupric bromide, which had remained standing for three weeks, were added two drops of a dilute solution (1 : 400) of methyl orange, and the greenish liquid was thoroughly shaken. Upon equally dividing the solution between two test-tubes, the most careful observation showed no difference in the color of the separate portions. To one tube was then added 0.05 c.c. of a twentieth normal solution of hydrobromic acid (= 0.2 milligram of bromine) and a change from green to gray was perfectly evident when the portions were again compared. A second equal addition of acid produced a purplish hue. The gray was of course due to the simultaneous presence of the red color of the acidified methyl orange, the yellow of the unchanged compound, and the blue of the copper bromide, and proved that some of the indicator had been acted upon by the acid: hence the solution could not have been basic in the first place. In a few words, the solution, containing about one and a half grams of cupric bromide, could not possibly have lacked more than 0.0002 gram of its normal weight of bromine. This being the case, a determination of the relative weights of copper and bromine in such a solution would form a sufficiently accurate basis for the calculation of the atomic weight of copper.

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* Berthemot, Ann. de Chim. et de Physique, 2d Series, xliv. 386 (1830); Löwig, Liebig's Handwört. Ch., iv. 713; Rammelsberg, Pogg. Ann., lv. 246; and many others.

Method of Analysis.

The bromine and copper were determined in separate weighed portions of the solution, according to usual methods. For the estimation of the former, the diluted cupric bromide was slowly added to a slight excess of pure argentic nitrate dissolved in one hundred and fifty cubic centimeters of hot water. In some of the determinations nitric acid was added to the silver nitrate before the precipitation, and in the other cases the acid was added afterward; but the difference in procedure produced no difference in result. The silver bromide settled readily, and was treated in the manner already described.*

The copper was determined in another weighed portion of the solution by electrolysis, after the complete expulsion of the bromine by means of nitric and sulphuric acids. One and a half to three grams of cupric bromide were used in each determination, and usually one part of nitric acid and two parts of sulphuric acid were taken to decompose one part by weight of the salt; but here again the relative quantities were varied without any perceptible effect upon the result. When the bromine and nitric acid had been expelled over the water bath, the residual copper sulphate and sulphuric acid were dissolved in a small quantity of water, and the whole transferred to the platinum crucible which was to serve as the negative electrode. It was found that within reasonable limits the size of the crucible and the dilution of its contents had no important effect upon the deposition of the copper, provided that the strength of the current was properly regulated. With six gravity cells and eighty ohms external resistance it was possible to deposit perfectly half a gram of copper in a coherent film from twenty-five cubic centimeters of solution. The positive electrode consisted in every case of a strong platinum wire fused into the centre of the watch-glass serving as a cover to the crucible. Twice before the completion of each electrolysis the liquid adhering to the lower surface of this lid was washed into the crucible, and the current was always maintained for at least thirty-six hours. Upon breaking the circuit, the sulphuric acid was at once wholly displaced by a stream of distilled water, and after washing by decantation with pure water, alcohol, and ether, the film was finally dried at 95° C. to perfectly constant weight. All the washings were collected in a large porcelain dish, carefully examined in order to be sure that no copper had been carried away, and after evaporation to small bulk tested with uniformly negative result for the presence of traces of metal in solution. It is almost needless to state, that, in every operation involving the quantitative transference of liquid, the original containing vessel was washed out with the most scrupulous care, and finally tested to prove the absence of any trace of its former contents.

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* Page 198 of this paper.

Below is the series of four results obtained from the first cupric bromide solution. About two weeks elapsed between the first and last determinations of this series.

PRELIMINARY RESULTS: FIRST SERIES.

Determination of Copper.

No. of Experiment.	$CuBr_2$ Solution taken.	Copper found (reduced to vacuum).	Copper in 25 grams Solution (to vac.).
	grams.	grams.	grams.
1	26.400	0.4397	0.4164
2	26.423	0.4401	0.4164
3	52.824	0.8799	0.4164
4	26.454	0.44075	0.4165
		Average . . .	0.41642

Determination of Bromine.

No. of Experiment.	$CuBr_2$ Solution taken.	AgBr found (reduced to vacuum).	Bromine in 25 grams Solution (to vac.).
	grams.	grams.	grams.
5	26.419	2.5995	1.0468
6	26.436	2.6018	1.0471
7	26.413	2.5996	1.0471
8	26.414	2.5990	1.0468
		Average . . .	1.04695

Atomic Weight of Copper.

From above results, if Ag : Br = 108.00 : 80.007, Cu = 63.644.
From results of previous paper, if Ag : Br = 108.00 : 80.007, Cu = 63.640.
According to Hampe, on same basis, Cu = 63.37±.

Since atomic weights are in any case relative, the ratio * Ag : Br = 108.00 : 80.007 will be assumed as the present standard of reference, for the sake of convenience and comparison with previous work. Later, all values will be translated into the various generally accepted standards.

The second series of analyses was made from the more dilute solution of a new sample of the salt, prepared in the same manner as the first, but perhaps somewhat less pure. The object was to seek further evidence of the constancy of the composition of dissolved cupric bromide, and it will be seen that the result agrees moderately well with the former one.

PRELIMINARY RESULTS: SECOND SERIES.

Determination of Copper.

No. of Experiment.	$CuBr_2$ Solution taken.	Copper found (reduced to vacuum).	Copper in 25 grams Solution (to vac.).
	grams.	grams.	grams.
9	77.875	0.8158	0.26190
10	51.891	0.5435	0.26185
		Average . . .	0.26187

Determination of Bromine.

No. of Experiment.	$CuBr_2$ Solution taken.	Silver Bromide found (reduced to vacuum).	Bromine in 25 grams Solution (to vac.).
	grams.	grams.	grams.
11	51.871	3.2114	0.65866
12	51.870	3.2113	0.65865
13	40.308	2.4957	0.65871
		Average . . .	0.65867

Atomic Weight of Copper 63.618

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* Although this ratio is not materially different from 108 : 80, we select it as the mean value of all the most accurate determinations.

It is certain that the hydrobromic acid used in making this preparation, notwithstanding the care taken in its manufacture, contained a trace of alkali from the glass retort used in distilling; and the presence of this impurity would tend to lower the observed atomic weight of copper. In order to correct this evil, and also in the hope that free hydrobromic acid might prevent the very slight formation of basic salt which invariably took place on the evaporation of water from the neutral salt, the attempt was made to crystallize the cupric bromide from acid solutions. The crystals were still basic, owing to the surface decomposition of exposed scales, but nevertheless two small distinct preparations of such crystals were dissolved, allowed to deposit their basic salt, and each analyzed for copper and bromine. Neither of these analyses was wholly satisfactory, but for the sake of completeness their final results are given below.

PRELIMINARY RESULTS: THIRD SERIES.

Solution of Crystals.

No. of Experiment.	Weight of Copper (reduced to vacuum).	Weight of AgBr (reduced to vacuum).	Atomic Weight Copper. AgBr = 188.007.
	grams.	grams.	
14 and 15	0.2500	1.4771	63.64
16 and 17	0.5473	3.2348	63.62

All the results thus far given were regarded merely as preliminary ones; and a complete series in which all possible care should be taken, both in preparation and analysis, remained still to be made. But before proceeding to the final determinations it was thought well to make several experiments with the object of proving the exactness of certain operations of the work. In the first place, two samples of the asbestos used for filtering were tested several times for constancy in weight, after heating to different temperatures; and the greatest loss of any one mat between 130° C. and 700° C. was found to be less than one tenth of a milligram.

In the next place the copper films of experiments 1 and 2 were heated in their crucibles to 500° C. in a stream of pure hydrogen, which was supplied through a curved tube and a perforated lid after the manner of Rose. The platinum rim left unprotected by the copper film was so small that absorption of hydrogen must have taken place only in unweighable quantities. No change in the weight of the copper was observed.

Finally, 0.3530 gram of purest electrolytic copper lost 0.00005 gram on heating to incipient redness in an atmosphere of hydrogen. After dissolving in nitric and sulphuric acids and electrolyzing precisely as usual, the recovered copper weighed 0.35305 gram, indicating a gain of only one tenth of a milligram over the lowest weight previously observed. This gain is not greater than a possible error in weighing; hence, as proof of the accuracy of the electrolytic method and the purity of the materials, the experiment leaves little to be desired.

II. FINAL DETERMINATIONS.

Preparation of Cupric Bromide.

In preparing cupric bromide for the final series of experiments it was decided to adopt a wholly new method, namely, the action of excess of bromine upon copper in the presence of water. Pure copper was prepared from a new source, the chemically pure sulphate from a noted German house, by the method which has so often been described.* The salt was freed from a possible trace of bismuth and iron by potassic hydrate in very dilute solution, precipitated from the concentrated filtrate by sulphuric acid, and after many re-crystallizations was finally twice successively decomposed by fractional electrolysis. The resulting copper was a very brilliant and beautiful substance; after being thoroughly washed and dried at 90°, it showed no trace of oxidation on standing three months.

The problem of the preparation of pure bromine has been admirably solved by Stas,† and the method adopted in the present case was largely based upon his, although differing from it in several important particulars. Sixty grams of potassic bromide in dilute solution were completely freed from a trace of iodine by two additions of a small quantity of bromine water, shaking out each time with successive portions of pure carbon disulphide until the two liquids in the separating funnel were alike colorless. After evaporation, the aqueous solution of potassic bromide was mixed with pure dilute sulphuric acid and pure powdered manganese dioxide, and the mixture was subjected to distillation from a glass retort over a water bath, into a glass condenser packed in ice. The manganese dioxide had previously been washed with an aqueous solution of bromine, pure water, hot dilute sulphuric acid, and finally with pure water again until neutral to litmus.

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* These Proceedings, xxii. 346, xxiii. 178; this paper, page 199.

† Stas's Untersuchungen, p. 158; Uebergesetzt von L. Aronstein, Leipzig.

Thirty-seven grams of bromine thus prepared were washed twice with water and distilled four times in two very small flasks with long side tubes, the bulbs being alternately packed in ice and immersed in hot water as they alternately served for condenser and retort. The neck of the one serving as the latter was stopped with a glass rod wrapped in fine asbestos, and this bulb was always cleaned and dried before being in its turn used as condenser. In this way bromine may be indefinitely redistilled with very little escape of vapor and without the least inconvenience.

The resulting bromine, although free from iodine, of course still contained an impurity of chlorine, which it is possible to remove by the solution of the whole mass in concentrated aqueous calcic bromide. The required salt was made by the addition of bromine to a mixture of milk of lime with sufficient ammonia water to prevent the formation of oxygen salts of calcium. The clear filtrate from this operation was evaporated to dryness, and the slight excess of lime was neutralized by means of pure hydrobromic acid. The calcic bromide thus formed was freed from iodine in the manner described in the case of the potassium salt, and a very small amount of the pure product served to dissolve all the bromine previously made. The intensely colored, heavy solution parted with some of its bromine on dilution, and with nearly all the remainder on gentle distillation.

Bromine thus prepared is absolutely free from chlorine as well as from iodine. After being twice more distilled, it was taken at once for the preparation of the bromide of copper used in the final determinations of the atomic weight. The combination of the halogen and the metal took place in a cooled flask containing water, and after its completion the slight excess of bromine — added to insure absence of cuprous bromide — was expelled by gentle evaporation to dryness in a glass dish. The nearly normal cupric bromide was then dissolved in a small amount of water, and the strong solution filtered through asbestos in a perforated crucible.

All experiments hitherto tried upon the salt had led to the conclusion that the solid alone loses bromine in the air, the solution being perfectly stable. If therefore it were possible suddenly to crystallize the salt and immediately to wash and dissolve it, we might hope to obtain a normal solution by a method which would insure perfect purity. This result was at last attained by the concentration of the dissolved cupric bromide, barely acidified with pure hydrobromic acid, to the consistency of syrup, — the containing vessel being left wholly undisturbed in vacuo for thirty-six hours. Upon agitation and cooling with ice, the resulting odorless, black supersaturated solution at once crystallized into a mass of brownish green needles, which were collected on a perforated crucible and washed three times with a very little water. These needles were wholly different in form and appearance from the black scales previously prepared: they were undoubtedly identical with those described by Berthemot and Löwig.* The dilute solution of these crystals deposited only a wholly insignificant amount of the basic bromide upon standing, and this small amount was undoubtedly formed by the rapid current of air drawn through the Gooch crucible. After remaining for more than a week longer there was no sign of further deposition, and the pure liquid was subjected to analysis, with the results given below.

METHOD OF ANALYSIS.

The copper was determined in the same manner as before, except that in experiment 18 the crucible serving as the negative electrode was previously coated inside with a thin film of copper, so that the external conditions before and after the analysis might be the same. The data of this experiment may perhaps make the understanding of the method more clear.

Experiment 18.

grams.
Weight of glass-stoppered flask with $CuBr_2$ solution = 93.872
Weight of glass-stoppered flask alone = 32.289
Weight of solution taken = 61.583

Corrected Weights. grams.
Crucible with copper before analysis = 36.5516
1st drying crucible with additional Cu after analysis = 37.2260
2d drying crucible with additional Cu after analysis = 37.22605
Gain of copper film = 0.6744
Correction to vacuum = 0.0000
Weight of copper found = 0.6744

Result.

$$\text{Weight of copper in 50 grams solution} = \frac{50 \times 0.6744}{61.583} = 0.54755$$

In precipitating the bromine from new portions of the solution, not only was the resulting silver bromide weighed, but also the silver required to form it; and this last value was determined according to two distinct methods. In the first place, the weight of silver required for a given weight of the copper bromide was calculated, and somewhat less than this amount was weighed out and dissolved in nitric acid in the manner before described. The cupric bromide was then cautiously added to the warm dilute solution, and the deficiency of silver made up by very careful titration with a solution containing one gram of silver to the litre.* After noting carefully this first value for the amount of silver required, a slight known excess of the standard solution was added, and the silver bromide was washed, collected, and weighed upon a perforated crucible, as before. The excess of silver in the filtrate was now carefully determined by means of a standard solution of ammonic sulphocyanide, using as a standard of colorimetric comparison solutions containing an equivalent amount of pure copper nitrate and small known amounts of silver nitrate. This second method of determining the amount of silver required to precipitate the bromine is not so accurate as the first, but is of value as a check upon the other. The most complete experiment tried is given in detail, as an example of the method.

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* Berthemot and Löwig, *loc. cit.*

Experiments 22 *and* 25.

		grams.
Glass-stoppered flask with $CuBr_2$ solution	=	47.711
Glass-stoppered flask alone	=	21.776
Cupric bromide solution taken	=	25.935

		Corrected Weights. grams.
Amount of silver dissolved (cor. to vac.)	=	0.9639
Amount of silver added in titration	=	0.0001
First value found for required Silver	=	0.9640
0.50 c.c. excess of $AgNO_3$ solution added to filtrate. Silver present	=	0.0005
Total weight of silver used	=	0.9645
Excess of silver was precipitated by 0.07 c.c. NH_4SCN solution. Corresponding silver	=	0.0007
Second value for required Silver	=	0.9638

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* For a further description of the method by Prof. J. P. Cooke, see these Proceedings, xvii. 18.

grams.

Weight of crucible + AgBr dried at 130° = 18.2516

“ “ “ “ 220° = 18.2516

“ Gooch crucible alone = 16.5738

“ AgBr in air = 1.6778

“ “ vacuo = 1.6779

Results.

Weight of silver bromide from 50 grams of solution = 3.2348

“ silver (average) for “ “ = 1.8583

“ bromine in 50 grams solution = 1.3765

“ Br calculated from AgBr $\left(\frac{80.007}{188.007}\right)$ = 1.3766

Following are the essential data of all the experiments made with the pure solution of crystallized cupric bromide. The results are expressed in the same terms as those given above, and from the combination of these figures a final average value for the atomic weight of copper may be readily deduced.

FINAL ANALYSES.

Determination of Copper.

No. of Experiment.	$CuBr_2$ Solution taken.	Copper found (reduced to vacuum).	Copper (red. to vac.) in 50 grams Solution.
	grams.	grams.	grams.
18	61.583	0.6744	0.54755
19	51.955	0.5689	0.54750
		Average . . .	0.54753

Determination of Bromine.

No. of Experiment.	$CuBr_2$ Solution taken.	Silver Bromide found (reduced to vacuum).	Bromine (red. to vac.) in 50 grams Solution.
	grams.	grams.	grams.
20	25.998	1.68205	1.3767
21	25.957	1.6789	1.3762
22	25.935	1.6779	1.3766
		Average . . .	1.3765

Determination of Silver.

No. of Experiment.	$CuBr_2$ Solution taken.	Silver required (red. to vac.).		Silver (red. to vac.) for 50 grams Solution.
		Direct Titration.	Sulphocyanide.	
	grams.	grams.	grams.	grams.
23	25.998	....	0.9664	1.8586
24	25.957	0.9645	....	1.8579
25	25.935	0.9640	0.9638	1.8583
		Average . . .		1.8583

Atomic Weight of Copper,

Calculated from the data given above, on the assumption that
Ag : Br = 108.00 : 80.007

Atomic Weight of Copper. [Br = 80.007.]

I. From Experiments 18 and 20 = 63.643
II. " " 18 " 21 = 63.664
III. " " 18 " 22 = 63.648
IV. " " 19 " 20 = 63.636
V. " " 19 " 21 = 63.657
VI. " " 19 " 22 = 63.641
Average = 63.648

[Ag = 108.00.]

VII. From Experiments 18 and 23 = 63.634
VIII. " " 18 " 24 = 63.659
IX. " " 18 " 25 = 63.645
X. " " 19 " 23 = 63.628
XI. " " 19 " 24 = 63.653
XII. " " 19 " 25 = 63.638
Average 63.643
Total average = 63.645

Highest value = 63.664
Lowest " = 63.628

Greatest variation from mean = ±0.018

If Ag = 108, result previously published = 63.640
If Ag = 108, accepted value (Hampe) = 63.37±

Each analytical result is combined with every other result above, in order that a better idea may be obtained of the variations of the figures. The combination of the averages of the three series of analyses would of course have given the same final average in a much more simple manner. Of the tabulated experiments, No. 23 is the least reliable, for the reasons before given; and rejecting values VII. and X. upon this ground the total average would become 63.648, with a "probable error" of about ±0.002.

The importance and value of the method of analysis, involving as it does the weighing of the silver used as well as of the argentic bromide formed, must be at once evident. Not only does the method give two wholly distinct classes of results for the atomic weight of copper, but besides this the relative weights of silver and bromine afford the sharpest possible test of the purity of the materials and the accuracy of the work. This method was first used by Professor Cooke in verifying the atomic weight of antimony, and he strongly insisted on the strength of the evidence thus furnished;* although the point has been strangely overlooked by commentators.

Percentage of Silver in Argentic Bromide.

From Experiments 20 and 23 = 57.454
" " 21 " 24 = 57.448
" " 22 " 25 = 57.447
Average = 57.450—
Average rejecting Exp. 23 as before = 57.448—
According to Stas = 57.445

Previous determinations made in this Laboratory by various experimenters have given values ranging from 57.442 to 57.450.

The agreement of the present value of the atomic weight of copper with the result which I previously published in these Proceedings † is a rather remarkable one, especially since the methods of work were wholly different in the two cases. The very slight difference between the preliminary and final results of this paper has already been explained, so that all the experiments which have been tried in this laboratory point to precisely the same figure.

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* These Proceedings, xvii. 19; also Huntington on Atomic Weight of Cadmium, these Proceedings, xvii. 28.

† Vol. xxiii. p. 180.

In this connection it is worthy of notice that H. Baubigny,* a recent experimenter upon the atomic weight of copper, dried cupric sulphate at 440° without evidence of the formation of basic salt, and from the weight of copper oxide produced by the ignition of this salt obtained the value 63.47 for the constant under discussion. Baubigny's experiments are too briefly described to be fairly discussed, but their evidence agrees with that of the results of Shaw † in pointing toward a higher value of the atomic weight of copper than that usually accepted.

In the critical review of the present investigation it must be remembered that three distinct methods have been used, the last two being united for the sake of convenience. The chief probable constant error in the first series, given in the two preceding papers, is the chance of a secondary reaction between the copper and the argentic nitrate; but the purity of the silver produced, the absence of the slightest gas evolution during the progress of the chemical action, and the total lack of effect of dilution upon the final result, alike point to the conclusion that no such secondary action took place. In the research upon cupric bromide the chief probable constant error which could raise the observed atomic weight of copper is the presence of basic salt in the solution, but the final crystallization of a neutral salt from an acid solution makes this chance very unlikely. Moreover, the basic salt was shown to be perfectly insoluble in water, and a direct experiment with methyl-orange proved the solution to be normal.

While no experimental knowledge can be said to be even relatively certain, and these with all other results are submitted only to be revised, and perhaps changed, by later experimentation, careful thought seems to show that the presumption is now upon the side of the later determinations of the atomic weight of copper.

During the last few years the atomic weights of antimony ‡ and of cadmium § have also been determined in this Laboratory, and have been referred to the same elements as those used in the present work. A statement of the final comparison might not be uninteresting.

$$\mathrm{Ag : Br : Sb : Cd : Cu} = 108.00 : 80.00+ : 120.00 : 112.31 : 63.64.$$

The collective results of the research must now be referred to the various different units of atomic weight usually adopted. Recently, an investigation* has been conducted here upon the atomic weight of oxygen, and since then many other investigators† have taken up the same subject, all but one‡ confirming the result of that work. In view of this fact, and also in the light of the recent recalculation of Stas's results,§ it seems not out of place to state the value of the atomic weight of copper upon the basis O = 15.87, as well as according to the usual standards.

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* Compt. Rend., xcvii. 854, 906.

† Phil. Mag., 5th Series, xxiii. 138.

‡ J. P. Cooke, *loc. cit.*

§ O. W. Huntington, these Proceedings, xvii. 28.

Atomic Weight of Copper.

If Ag = 108.00	From [Cu : 2 Ag]	Cu = 63.640
	From [$CuBr_2$: 2 AgBr]	Cu = 63.648
	From [$CuBr_2$: 2 Ag]	Cu = 63.643
	Average	= 63.644
If Ag = 107.93	(O = 16.000)	Cu = 63.60
If Ag = 107.675	(Clarke)	Cu = 63.45
If Ag = 107.66	(Meyer and Seubert)	Cu = 63.44
If Ag = 107.06	(O = 15.87)	Cu = 63.09

In conclusion, the writer would express his deep sense of obligation to the kind friends whose interest and advice have so materially assisted the progress of the investigation.

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* Cooke and Richards, these Proceedings, xxiii. 149 and 182. Result, O = 15.87.

† Lord Rayleigh, Roy. Soc. Proc., xliii. 356 (1888); W. A. Noyes, Am. Chem. Journal, xi. 155, xii. 441; E. W. Morley, results as yet unpublished. Also discussions by Crafts, Compt. Rend., cvi. 1662, and many others.

‡ Keiser, Am. Chem. Journal, x. 249. Result, O = 15.95.

§ J. D. Van der Plaats, Chem. News, liv. 186. These results point to a value of oxygen between 15.87 and 15.89.